PCT/CA 03/02002
19 FEBRUARY 2004 19.02.04

PA 1111007

THE UNITED STATES OF AMERICA

TO ALL TO WHOM THESE PRESENTS SHALL COME:

UNITED STATES DEPARTMENT OF COMMERCE

United States Patent and Trademark Office

REC'D 10 MAR 2004
WIPO PCT

January 05, 2004

THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A FILING DATE UNDER 35 USC 111.

APPLICATION NUMBER: *60/436,022*
FILING DATE: *December 23, 2002*

PRIORITY DOCUMENT
SUBMITTED OR TRANSMITTED IN COMPLIANCE WITH RULE 17.1(a) OR (b)

By Authority of the
COMMISSIONER OF PATENTS AND TRADEMARKS

M. K. Hawkins

M. K. HAWKINS
Certifying Officer

Please type a plus sign (+) inside this box → [+]

12 60436022 PTO/SB/16 (2-98)

Approved for use through 01/31/2001. OMB 0651-0037
Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

12/23/02

A PROV

J1040 U.S. PTO 60/436022

PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53 (c).

INVENTOR(S)

Given Name (first and middle [if any])	Family Name or Surname	Residence (City and either State or Foreign Country)
Nicholas	PARSON	Banbury, England
Alan	GRAY	Banbury, England
Pierre H.	MAROIS	Kingston, Ontario, Canada
Thiagarajan	RAMANAN	North Royalton, Ohio

☐ Additional inventors are being named on the ___ separately numbered sheets attached hereto

TITLE OF THE INVENTION (280 characters max)

ALUMINUM ALLOY TUBE AND FIN ASSEMBLY FOR HEAT EXCHANGERS HAVING IMPROVED CORROSION RESISTANCE AFTER BRAZING

CORRESPONDENCE ADDRESS

Direct all correspondence to:

☐ Customer Number [ ] → Place Customer Number Bar Code Label here

Type Customer Number here

OR

[xx] Firm or Individual Name	Christopher C. Dunham COOPER & DUNHAM LLP				
Address	1185 Ave. of the Americas				
Address					
City	New York	State	N.Y.	ZIP	10036
Country	USA	Telephone	(212) 278-0400	Fax	212 391-0525

ENCLOSED APPLICATION PARTS (check all that apply)

[xx] Specification Number of Pages: 12

☐ Small Entity Statement

☐ Drawing(s) Number of Sheets: 0

[xx] Other (specify): Express Mail Label No. EL 006 422 497 US

METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT (check one)

[xx] A check or money order is enclosed to cover the filing fees

☐ The Commissioner is hereby authorized to charge filing fees or credit any overpayment to Deposit Account Number: 03-3125

FILING FEE AMOUNT ($): 160.00

The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.

[xx] No.

☐ Yes, the name of the U.S. Government agency and the Government contract number are: ___

Respectfully submitted,

SIGNATURE Christopher C. Dunham

Date 12/23/02

TYPED or PRINTED NAME Christopher C. Dunham

REGISTRATION NO. (if appropriate) 22,031

TELEPHONE (212) 278-0400

Docket Number: 68738 CCD

USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT

60436022 . 122302

Dkt. 68738 CCD

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants : Nicholas Parson et al.
Serial No.: not yet assigned
Filed : currently herewith
For : ALUMINUM ALLOY TUBE AND FIN ASSEMBLY FOR HEAT EXCHANGERS HAVING IMPROVED CORROSION RESISTANCE AFTER BRAZING

EXPRESS MAIL LETTER OF TRANSMITTAL

1185 Ave. of the Americas
New York, N.Y. 10036
December 23, 2002

Hon. Commissioner of Patents and Trademarks
Washington, D.C. 20231

S I R:

I hereby certify that the above-identified Provisional application (consisting of **12** pages, provisional application cover sheet + fee check for **$160**) is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 C.F.R. §1.10 on the date indicated below, and is addressed to the Assistant Commissioner for Patents.

Mailroom Employee
Depositing Express Mail Material

Express Mail mailing label No. **EL 006 422 497 US**

Date of Deposit: DECEMBER 23, 2002

Christopher C Dunham
Attorney for Applicants
Christopher C. Dunham,
Reg. No. 22,031
COOPER & DUNHAM LLP
Tel. (212) 278-0400

ALUMINUM ALLOY TUBE AND FIN ASSEMBLY FOR HEAT EXCHANGERS HAVING IMPROVED CORROSION RESISTANCE AFTER BRAZING

Field of the Invention

This invention relates to extruded aluminum alloy products of improved corrosion resistance. It particularly relates to extruded tubes for heat exchangers having improved corrosion resistance after brazing when paired with a compatible finstock.

Background of the Invention

Commercially produced aluminum microport tubing for use in brazed applications is generally produced in the following manner. The extrusion ingot is cast and optionally homogenized by heating the metal to an elevated temperature and then cooling in a controlled manner. The ingot is then reheated and extruded into microport tubing. This is generally thermally sprayed with zinc before quenching, drying and coiling. The coils are then unwound, straightened and cut to length. The tubes obtained are then stacked with corrugated fins clad with filler metal between each tube and the ends are then inserted into headers. The assemblies are then banded, fluxed and dried.

The assemblies can be exposed to a braze cycle in batch or tunnel furnaces. Generally, most condensers are produced in tunnel furnaces. The assemblies are placed on conveyor belts or in trays that progress through the various sections of the furnace until they reach the brazing zone. Brazing is carried out in a nitrogen atmosphere. The heating rate of the assemblies depends on the size and mass of the unit but the heating rate is usually close to 20°C/min. The time and temperature of the brazing cycle depends on the part configuration but is usually carried out between 595 and 610°C for 1 to 30 minutes.

A difficulty with the use of aluminum alloy products in corrosive environments, such as automotive heat exchanger tubing, is pitting corrosion. Once small pits start to form, corrosion actively concentrates in the region of the pits, so that perforation and failure of the alloy occurs much more rapidly than it would if the corrosion were more general. With such a large cathode/anode area ratio, the dissolution rate at the active sites is very rapid and tubes manufactured from conventional alloys can perforate rapidly, for example in 2-6 days in the SWAAT test.

Zinc coating applied to the tube after extrusion acts to inhibit corrosion of the tube itself. However during the braze cycle, the Zn layer on the extruded tube starts to melt at around 450°C and once molten, is drawn into the fillet/tube joint through capillary action. This occurs before the Al-Si cladding (fin material) melts at approximately 570°C and as result the tube-to-fin fillet becomes enriched with Zn, rendering it electrochemically sacrificial to the surrounding fin and tube material. A problem with thermally spraying with zinc before brazing is therefore that the braze fillets become zinc enriched and tend to be the first parts of the units to corrode. As a result, the fins become detached from the tubes, reducing the thermal efficiency of the heat exchanger. In addition to these physical effects, any enrichment of the fillet region with Zn has the effect of reducing the thermal conductivity of the prime heat transfer interface between the tube/fin. There is also a desire to move away from the use of zinc for cost savings and for workplace environment reasons.

In an assembly of brazed tubes and fins, it has been found to be advantageous to have the fins corrode first and thereby galvanically protect the tubes. Most fin alloys used with extruded tubes are clad alloys where the core alloys are either 3XXX or 7XXX series alloy based and contain some zinc to make them electronegative, and thereby provide this type of

protection. By making the fin sufficiently electronegative, the tubes to which the fins are brazed can be protected, in this way, if the zinc content of the fin is raised sufficiently. However, this has a negative impact on the thermal conductivity of the fin and on the ultimate recyclability of the unit. Furthermore, if the fin material is too electronegative it can corrode too fast and thereby compromises the thermal performance of the entire heat exchanger. Corrosion potential and the difference between corrosion potential of tube and fin have been frequently used to select tube and fin alloys to be galvanically compatible (so that the fin corrodes before the tube). This technique serves to give an approximate galvanic ranking. In order to obtain a true determination of the performance of such combinations it has been found that a measurement of the direction and magnitude of the galvanic current permits a better determination of ultimate performance. Little attempt has been made to optimize the tube-fin combination in heat exchangers based on extruded tubes through the use of appropriate alloys alone, the use of zinc cladding being widely used instead. One constraint on such optimization is that it still also must be possible to extrude the tubes without difficulty.

Anthony et al., U.S. Patent 3,878,871, issued April 22, 1975, describes a corrosion resistant aluminum alloy composite material comprising an aluminum alloy core containing from 0.1 to 0.8% manganese and from 0.05 to 0.5% silicon, and a layer of cladding material which is an aluminum alloy containing 0.8 to 1.2% manganese and 0.1 to 0.4% zinc.

Sircar, U.S. Patent 5,785,776, issued July 28,1998, describes a corrosion resistant AA 3000 series aluminum alloy containing controlled amounts of copper, zinc and titanium. It has a titanium content of 0.03 to 0.30%, but this level of

titanium raises the pressures required for extrusion, which will ultimately lower productivity.

In Jeffrey et al., U.S. Patent 6,284,386, issued September 4, 2001, extruded aluminum alloy products having a high resistance to pitting corrosion are described in which the alloy contains about 0.001 to 0.3% zinc and about 0.001 to 0.03% titanium. The alloys preferably also contain about 0.001 to 0.5% manganese and about 0.03 to 0.4% silicon. These extruded products are particularly useful in the form of extruded tubes for mechanically assembled heat exchangers.

It is an object of the present invention to provide brazed extruded aluminum alloy tubing for heat exchangers having adequate corrosion resistance without special treatments, such as thermal spraying of the surface with zinc, and also being galvanically compatible with fins joined thereto.

It is a further object of the present invention to provide a brazed heat exchanger assembly consisting of extruded tubing and fins in which the tubing alloy is optimized to minimize self corrosion and so that the heat exchanger is protected from overall corrosion by a slow corrosion of the fins.

Summary of the Invention

The present invention in one embodiment relates to an aluminum alloy for an extruded heat exchanger tube comprising 0.4 to 1.1% by weight manganese, preferably 0.6 to 1.1% by weight manganese, up to 0.01% by weight copper, up to 0.05% by weight zinc, up to 0.2% by weight iron, up to 0.2% by weight silicon, up to 0.01% by weight nickel, up to 0.05% by weight titanium and the balance aluminum and incidental impurities.

Further embodiments comprise an extruded tube made from the above alloy and such a tube when brazed.

In a yet further embodiment, the invention relates to a brazed heat exchanger comprising joined heat exchanger tubes and heat exchanger fins, where the tubes are extruded tubes made from a first alloy comprising the aluminum alloy described above and the fins are formed from a second alloy comprising an aluminum alloy containing about 0.9 to 1.5% by weight Mn and at least 0.5% by weight Zn, or an aluminum alloy of the AA 3000 series, e.g. an aluminum alloy of the AA 3003 type, with this second alloy further containing at least 0.5% by weight zinc.

It appears that the above unique combination of alloying elements for the tubes gives unexpectedly good self anti-corrosion results for the tubes without the need for any coating of zinc. Also by keeping the manganese content of the tube alloy within 0.8% by weight of that of the fin, the fin remains sacrificial, thus protecting the tube and the galvanic corrosion current remains relatively low so that the fin is not corroded so rapidly in service that the thermal performance of the assembly is compromised.

The above combination of aluminum alloy fins and extruded tubes when assembled and furnace brazed exhibit a very slow and uniform corrosion of exposed fin surfaces, rather than localized pitting of the tube. The invention is particularly useful when the tubes are microport tubes and the assembly has been furnace brazed in an inert atmosphere.

<u>Description of the Preferred Embodiments</u>

According to a preferred feature, the fin alloy has less than about 0.05% by weight of copper to make it galvanically compatible with the amount of copper in the extruded tube.

When a brazed heat exchanger is manufactured with these alloy limitations, the heat exchanger tubes can be used without a zincating treatment. The heat exchanger tube does not show self-corrosion in areas remote from the fins (e.g. in

between the header and fin pack), and the fins corrode before the tubing but at a rate sufficiently slow to ensure performance of the heat exchanger is maintained for extended periods of time.

Manganese in the tube alloy in the amount specified provides for good self-corrosion protection, along with adequate mechanical strength yet still permits the tubing to be easily extruded. If the manganese is less than 0.4% by weight the tube itself can corrode when coupled with the fin, and if greater than 1.1% by weight the extrudability of the material is adversely affected. When the manganese levels in the tube and fin differ by less than 0.8% by weight (and preferably by less than 0.6% by weight) then the fin remains sacrificial to the tube, the corrosion current remains low and therefore the rate of fin corrosion is acceptable. To meet compatibility requirements under a broad range of conditions, it is preferred that the manganese level in the tube therefore be greater than 0.6% by weight.

A particularly preferred tube alloy composition contains 0.9 to 1.1% by weight of manganese, since this represents an alloy that can be extruded into the desired tubes whilst minimizing the manganese concentration differences between tube and fin.

The relative manganese content of the fin and tube alloys can also be expressed by the measured galvanic corrosion current. The measured galvanic corrosion current from the fin to the tube must preferably exceed +0.05 microamps per square centimeter when measured via ASTM G71-81.

The zinc content of the tube must be maintained at a low level to ensure that the fin remains sacrificial to the tube. Even relatively low levels of zinc can alter the galvanic corrosion current and thereby alter this sacrificial relationship. The zinc must therefore be kept at less than 0.05% by weight, more preferably at less than 0.03% by weight.

Iron, silicon, copper and nickel all contribute to self-corrosion of the tube and therefore must be below the stated levels. In addition, iron above 0.2% by weight results in poor extrusion surface quality.

Titanium additions to the alloy make it difficult to extrude and therefore the titanium should be less than 0.05% by weight.

The alloy billets are preferably homogenized between 580 and 620°C before extrusion into tubes.

Example:

Tests were conducted using the alloys listed in Table 1 below:

Table 1

Alloy	Cu	Fe	Mg	Mn	Ni	Si	Ti	Zn
A	<.001	0.09	<.001	0.22	<.001	0.058	0.017	0.004
B	0.014	0.07	<.001	0.23	<.001	0.07	0.008	0.17
C	0.015	0.51	0.021	0.33	0.001	0.32	0.014	0.007
D	0.001	0.08	<.001	0.98	0.002	0.064	0.014	0.18
E	0.015	0.09	<.001	1.00	<.001	0.07	0.007	0.18
F	<.001	0.08	<.001	0.98	0.001	0.071	0.008	0.005
G	0.006	0.11	0.001	0.42	0.001	0.078	0.023	0.027
H	0.006	0.10	0.002	0.63	0.001	0.079	0.021	0.029

These alloys were cast into 152 mm diameter billets. Alloy C was a commercial 3102 alloy. The billets were further machined down to 97 mm in diameter and homogenized between 580 and 620°C. They were then extruded into tubes. Samples of the tubing were subjected to a simulated brazing process and then subjected to a SWAAT test using ASTM standard G85 Annex 3 and galvanic corrosion currents were measured against a standard finstock material manufactured from AA3003 alloy containing 1.5% by weight added zinc and clad with AA4043 alloy that had also been given a simulated braze cycle, in accordance with ASTM G71-81. The results are shown in Table 2 below:

Table 2

Alloy	SWAAT life (days)	Galvanic corrosion current ($\mu A/cm^2$)*
A	56	-3.2
B	<20	
D	56	-2.4
E	<20	
F	56	0.2
G		3.1
H		5
F unhomogenized	21	
C zincated	56	-26.9

* +ve corrosion current = current flow from fin to tube
-ve corrosion current = current flow from tube to fin

The results of a test carried out on a zincated 3102 tube (e.g. Alloy C, Extruded and zincated) are shown for comparison. In Table 2, a SWAAT life of 56 days indicated no perforation of the tube by self-corrosion and a positive galvanic corrosion current indicates that the fin corrodes preferentially. A small value indicates a low rate of corrosion. A sample of alloy F was also extruded without homogenization and subjected to a SWAAT test.

Alloys A, D have compositions outside the claimed range. They nevertheless show excellent SWAAT performance indicating that for self-corrosion these alloys would be also be acceptable even when the Mn is less than the range of this invention. It is believed that this is a result of the low Cu, Fe and Ni in these alloys. The amount of Mn present has no significant effect on the self-corrosion behaviour. However, the galvanic corrosion current is unacceptable for these compositions. This is believed to be due to manganese levels that are too low in one case and zinc levels that are too high in the other. Both these elements are important in ensuring acceptable performance of the fin-tube galvanic couple.

Alloys B and E have copper outside the desired range and show poor SWAAT results, indicating that alloys with such a copper level would suffer from excessive self-corrosion, whether or not the manganese composition met the requirements.

Alloy D has a zinc level that exceeds the desired range and shows that although the manganese level is within the desired range, the fin-tube galvanic corrosion current is negative and the tube would therefore corrode first. The self-corrosion performance (SWAAT test) is acceptable, but because of the fin-tube galvanic corrosion, the overall assembly would fail.

Alloys F, G and H are alloys lying within the claimed range. Alloy F exhibits acceptable performance on all aspects. Alloys G and H show good galvanic corrosion behaviour, and lack any significant levels of elements that would give poor SWAAT performance.

Alloy F in un-homogenized condition however, shows unacceptable SWAAT performance indicating that homogenization of the product is preferable.

Finally Alloy C was a standard tube alloy and was tested in zinc-coated form. As expected this gave good SWAAT performance, since the zinc overcomes the negative effects of elements such as copper. However, the galvanic corrosion current indicates a poor performance of the fin-tube couple. Alloy C had manganese less than the desired range and the zinc coating introduces levels of zinc that are detrimental to galvanic corrosion current as well.

Claims:

1. An aluminum alloy for heat exchanger tubing comprising 0.4 to 1.1% by weight manganese, up to 0.01% by weight copper, up to 0.05% by weight zinc, up to 0.2% by weight iron, up to 0.2% by weight silicon, up to 0.01% by weight nickel, up to 0.05% by weight titanium and the balance aluminum and incidental impurities.

2. An aluminum alloy according to claim 1 which has been homogenized at a temperature of between 580 and 620°C

3. An aluminum alloy according to claim 1 which has been extruded into tubing and brazed.

4. Brazed heat exchanger tubing formed from an aluminum alloy comprising 0.4 to 1.1% by weight manganese, up to 0.01% by weight copper, up to 0.05% by weight zinc, up to 0.2% by weight iron, up to 0.2% by weight silicon, up to 0.01% by weight nickel, up to 0.05% by weight titanium and the balance aluminum and incidental impurities.

5. A brazed heat exchanger assembly comprising joined heat exchanger tubes and heat exchange fins wherein the tubes are formed of a first aluminum alloy comprising 0.4 to 1.1% percent by weight manganese, up to 0.01% by weight copper, up to 0.05% by weight zinc, up to 0.2% by weight iron, up to 0.2% by weight silicon, up to 0.01% by weight nickel and the balance aluminum and incidental impurities and the fins are formed of a second aluminum alloy selected from the group consisting of an alloy comprising 0.9 to 1.5% by weight manganese and an alloy of the AA 3000 series, said second aluminum alloy further containing at least 0.5% by weight zinc, whereby the brazed tubes exhibit good self corrosion

protection and the fins are galvanically sacrificial relative to the tubes.

6. A brazed heat exchanger assembly according to claim 5 wherein the difference between the manganese content of the first aluminum alloy and the manganese content of the second aluminum alloy is less than 0.8% by weight.

7. A brazed heat exchanger assembly according to claim 5 wherein the second aluminum alloy contains less than 0.05% by weight copper.

8. A brazed heat exchanger assembly according to claim 5 wherein the AA 3000 series alloy is an AA 3003 alloy.

9. A brazed heat exchanger assembly according to claim 6 where the galvanic current from fin to tube is greater than +0.05 microamps per square centimeter.

10. A brazed heat exchanger assembly according to claim 5 where the first aluminum alloy contains between 0.6 and 1.1% by weight manganese.

11. A brazed heat exchanger assembly according to claim 5 where the first aluminium alloy contains between 0.9 and 1.1% by weight manganese.

Abstract

Extruded tubes for heat exchangers have improved corrison resistance when used alone and when part of a brazed heat exchanger assembly with compatible finstock. The tubes are formed from a first aluminum alloy comprising 0.4 to 1.1% by weight manganese, up to 0.01% by weight copper, up to 0.05% by weight zinc, up to 0.2% by weight iron, up to 0.2% by weight silicon, up to 0.01% by weight nickel, up to 0.05% by weight titanium and the balance aluminum and incidental impurities. The fins are formed from a second aluminum alloy containing 0.9 to 1.5% by weight manganese or an alloy of the AA 3000 series, this second aluminum alloy further containing at least 0.5% by weight zinc.